Development of laser fluorometer system for CDOM measurements

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Abstract: The colored fraction of dissolved organic matter, CDOM, directly influences water optical properties and spectral quality, playing an important role in aquatic ecosystems, optical remote sensing and carbon circulation in the sea. Measuring in situ CDOM absorption coefficient, however, is difficult because it requires prefiltration of water samples. An analytical laboratory and field instrument for fast diagnosis of chromophoric dissolved organic matter (CDOM) in water was developed. The laser fluorometer was integrated with spectral fluorescent signature (SFS) analysis of the laser stimulated emission excited at 405 nm and hyper spectra for surveillance of CDOM. CDOM and water Raman scattering components were derived from the laser stimulated emission spectra measured in the laboratory and field conditions with SFS technology, which added to analytical Lidar sensing the capability of detecting and identifying trace substances in a variety of targets in the presence of other background matters responding to optical excitation with overlapping signals. The influence of temperature change on CDOM fluorescence data in water was investigated in laboratory, and a temperature calibration method was employed for calibrating fluorometer data. Laboratory and in-situ studies with the laser fluorometer in the East China Sea (ECS) in April 2013 were carried out. Significant and positive correlation in the ECS was observed between CDOM absorption measurements and CDOM fluorescence (R^2=0.83). The result demonstrated the possibilities of CDOM monitoring in real time based upon the laser fluorometer.

Key words: laser induced fluorescence; spectroscopy; Raman

激光诱导荧光装置用于海水可溶性有机物测量

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摘　要：水体可溶性有机物(也叫黄色物质,CDOM),直接影响水体光学特性和遥感光谱特征,在水体生态系统、光学遥感、海洋碳循环中都发挥重要的作用。针对现有水体黄色物质(CDOM)常规测量需要对水样进行过滤等耗时耗力预处理过程,研制了一种水体黄色物质快速测量的可用于实验室及野

外分析的激光诱导荧光仪,该仪器集成了 405 nm 激光激发、高光谱接收和特征荧光光谱解析技术,使得激光雷达能够从各种成分的叠加信号中分离和确认出特定组分。此外,在实验室测量和分析了温度对于 CDOM 荧光光谱的影响,并提出了一种荧光数据的温度校正算法。该仪器在中国东海 2013 年 4 月的测量结果与常规仪器测量结果具有显著的相关性 (R^2=0.83),揭示了激光诱导荧光技术在 CDOM 实时监测上的应用潜力。

关键词: 激光诱导荧光; 光谱学; 拉曼

0 Introduction

Chromophoric dissolved organic matter (CDOM), also known as yellow substance or Gelbstoff, is an important component in governing light propagation in coastal and open ocean waters[1]. The optical properties of CDOM absorption complicate the use of chlorophyll a retrieval algorithms that are based on remotely sensed ocean color[2] and the development of phytoplankton production models[3]. Although CDOM strongly influences ocean optical properties, remotely sensed spectra, and biogeochemical processes, dynamics of CDOM in diverse aquatic environments remain largely undefined due partially to a sparse global database of CDOM absorption. Limited availability of such data is related to a lack of highly sensitive and portable optical systems that can provide measurements at sea [4]. Measuring in situ CDOM absorption coefficient, however, is difficult because it requires prefiltration of water samples. Relative to common absorption measurements, fluorescence measurements can be acquired more rapidly and with greater sensitivity. Measuring the CDOM in natural waters using its fluorescence signal is extremely useful in a variety of marine and freshwater applications. Active fluorescence analysis based on the measurements of the laser-induced water emission retrieves qualitative and quantitative information about the in-situ fluorescent constituents. Many shipboard, shore-based, and airborne laser fluorosensors have been developed for analyzing of natural aquatic environments. Apart from detecting oil pollution [5], LIF technology were used to measure phytoplankton abundance and describe phytoplankton communities [6] and characterization of CDOM [7]. Furthermore, LIF Lidar is also able to provide information on water transparency and turbidity[8]. Miniaturized transmitting-receiving system for laser detection was designed by Han Wei and Zheng Xiang etc[9] and Raman spectroscopy measurement system base on shifted excitation method using two laser diodes with different wavelengths was designed [10]. In the past years, water Raman(inelastic) scattering of a laser emission on water molecules was often used to normalize fluorescence[11]. To analyze spectral complexity, spectral fluorescent signature (SFS) technique was proposed, which added to analytical Lidar sensing the capability of detecting and identifying trace substances in a variety of targets in the presence of other background matters responding to optical excitation with overlapping signals [12], Gaussian fitting function(s) was used by Zhao Nanjing in 2005[13] and Xue Zechun in 2011[14] for de-convolute overlap spectral components, radial basis function networks was developed by Li Hongbin in 2005 [15], and the Pearson′s IV function (s) was introduced by Chekalyuk and Alexander to de-convolute spectral in 2008[16]. Recently, temperature effects on fluorescence were studied and corresponding temperature compensation algorithms for fluorometer were proposed[17], temperature compensation is a necessary and important aspect of CDOM monitoring using in situ fluorescence sensors. C.J. Watras and P.C. Hanson used a temperature compensation method for the C3 Submersible Fluorometer(Turner Designs, Inc.)

and the SeaPoint UV Fluorometer (SeaPoint Sensors, Inc.)[18].

Nowadays, most current commercial fluorosensors used UV LEDs and xenon lamps as the CDOM excitation lamp, and several shipboard and airborne laser fluorosensors have been developed, some commercially available field fluorometers use predefined multi-channel spectral detector to detect echo-signal, it is not suitable to ensure reliable assessment of complex fluorescent constituents in waters; some of them can′t provide flow-through measurements during the curies; CDOM fluorescence usually diminishes with increasing temperature, but there are very few fluorescence instruments to apply temperature compensation method to calibrate the fluorescence data in marine applications. Due to these issues, a new field instrument, the laser fluorometer system for CDOM measurements was developed. Our former field and laboratory experience measuring CDOM led us to design a LIF apparatus with simplicity and flexibility as its key characteristics. It was portable enough to be emplaced in shipboard and shore-based settings (Fig.1). A cabinet violet laser with lower power consumption was used to excite fluorescence and a hyper-spectral CCD camera was integrated to get broad high-resolution spectral fluorescence signal. It has several advantages: (1) the systematic framework was simple and flexible. It was easier to alter one certain part of the system (laser wavelength, or spectral detector etc.) to meet the specific needs; (2) discrete and underway flow-through sample measurements were provided, the experimental apparatus in this paper supplied high spatial resolution measurements with flow-through instrument (Fig.1(b)); (3) a water filter module was used to leach most particulate matter (phytoplankton, suspended sediment etc.). It was less effective to extract CDOM spectral component in case−II waters when the water spectral is complex, in order to improve the sensitivity and simplify spectral de-convolution, a water filter module was employed; (4) a

temperature compensation approach was used for calibrating fluorometer data. The laboratory and field experiments demonstrated the laser fluorometer system as an effective integrated tool for CDOM monitoring.
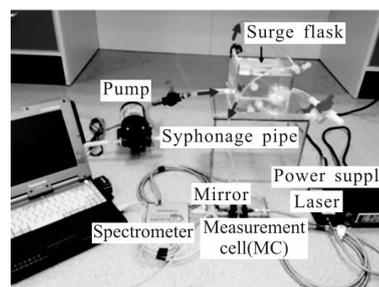
(a) Instrument schematic diagram
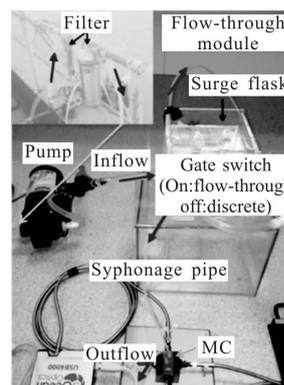
(b) Flow-through measurements schematic diagram

Fig.1 Instrument configured for the discrete and flow-through measurements

1 Data and methods

1.1 Instrument and methods

A combination of laser fluorometer, on-site SFS technique and temperature calibration algorithm for CDOM fluorescence was used for CDOM assessment in the present study. A simple and flexible analysis instrument for fluorescence spectroscopy induced by violet laser is designed for this study. The system is composed of an excitation source module based on micro-crystal violet laser, a laser driving and controlling module, a measurement cell (MC), a water filter module, and a spectroscopy-detecting module. A diagram of the laser fluorometer instrument is presented in Fig.2.
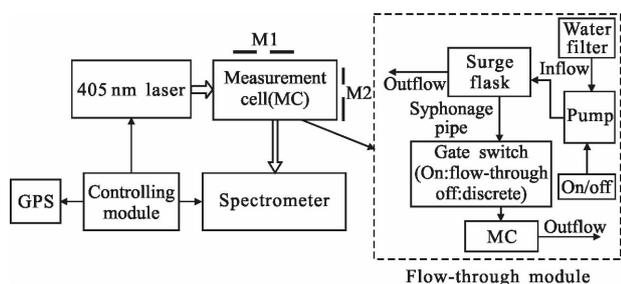
Fig.2 Block diagram of the laser fluorometer instrument

LD−pumped Q−switch microchip solid-state laser (MM −405 −100, Boson Tech), which emits at the wavelength of 405 nm and pulse duration (7 ns), with high peak power (greater than 10 kW), low power consumption (about 10 W), and high pulsed repetition frequency rate (greater than 10 kHz), is selected as the excitation source. The signal noise ratio (SNR) of fluorescence spectroscopy instrument can be increased by using high pulsed repetition frequency laser. The laser driving and controlling module mainly consists of two parts: power controlling circuit and temperature controlling circuit. The module is to provide stable power and temperature to the laser source. The sample pool is made from quartz, of which the size is 12.5 mm×12.5 mm×45 mm. The length of the internal optical path of sample space is 10 mm. Its four sides are polished and transparent. The dichroic mirrors, M1 and M2 (74−msp, Ocean Optics), reflect the laser and fluorescence beams from the other two-pass sides back to the MC to increase signal intensity. The LSE is collected with a high-sensitivity hyper-spectral fluorescence spectrometer (USB4000 −FL, Ocean Optics), preconfigured with an L4 Detector Collection Lens to increase light-collection efficiency and reduce stray light. The spectrometer covers the wavelength range of 360 −1 000 nm. During measurements, the water flow, supplied by the ship-board sampling pump, after passed through a 5 μm nuclepore membrane water filter, then passed through the input water connector into a surge flask. The effects of most algae and suspended solids spectral were excluded by the filter. Syphonage pipes were used to make water flow from surge flask into MC. A gate switch was used to control the measurement, when the gate switch was on, it switched to flow-through measurement, when the gate switch was off, it switched to discrete measurement. After measurements, the water exits through the discharge connector. Every recorded LIF spectrum is accompanied by recorded data of GPS coordinates and background signature (BN). We have used a shipboard GPS system (HM−1817, Garmin) and import coordinates and time. The SpectraSuite software (Ocean Optics software, Inc.) was used to record the spectra and GPS coordinates at the same time. B_N is corrected after every measurement. An example of spectra using B_N − corrected method is presented in Fig.3.
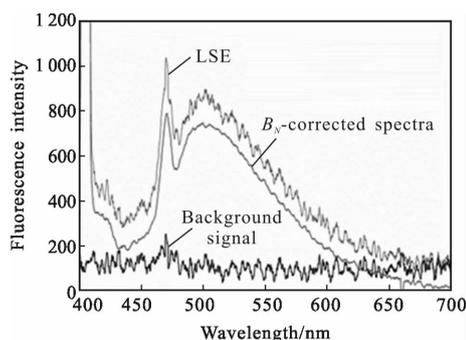

Fig.3 An example of spectra using BN−corrected method

1.2 Spectra

The SFS topology (spectral "fingerprint") serves as substance identifier, while the fluorescence intensity is used as a measure of substance quantity. The SFS is recorded as a multi-dimensional matrix of intensity and spectral parameters. Various organic compounds are manifested in such a matrix as specific structural singularities representing the SFS. With the SFS technique, the task of bio-chemical analysis becomes an issue of recognition and de-convolution of spectral images. The SFS analysis of LSE spectral measurements is based on linear amplitude scaling of the basic spectral components to provide the best fit of the spectrum resulting from their summation to the LSE signal in the selected spectral range. A set of the SFS

spectral components was derived from the LSE spectra measured in the laboratory and field conditions.

In this paper, elastic scattering spectra was cut off by a high-pass function and phytoplankton was filtered out by a water filter. So the LSE spectra were focusing on water Raman scattering and CDOM spectral component.

Gaussian function（s）of the least squares method was used for LSE spectral de-convolution to retrieve analytical approximations of the basic spectral components to describe the asymmetrical spectral shape of the constituent emission bands:

$$y = y_0 + \sum_{i}^{n} \frac{A_i e^{\frac{-4\ln(2)(x_i - xc_i)^2}{w_i^2}}}{w_i \sqrt{\frac{\pi}{4\ln(2)}}} \tag{1}$$

Here, y_0, A_i xc_i, and w_i are the parameters that define the base line, amplitude, center, and width, respectively, of the Gaussian band of the basic spectral components.

Gaussian function can be used to express parameters of shape, peak height and peak position, among others in spectra, with a clear physical meaning. It is feasible as the basic function of spectral curve fitting method. In the process of actual fitting, we do not require strictly fitting curve through all points, and only require through most points with a standard minimum fitting error; a least square′s approximation is often used for the best fitting curve. For a spectral curve, we can isolate a variable number of spectral components, according to the number of aquatic constituents we recognized. Recognition of aquatic constituents in the spectral image is indispensable for de-convolution, and the result of recognition gives the spectral components physical meaning. Figure 4 shows the de-convolution result of spectra with different numbers of spectral components. Figure 4(a) and Fig.4(b) demonstrate that the number of recognized aquatic components directly influenced the result of de-convolution.
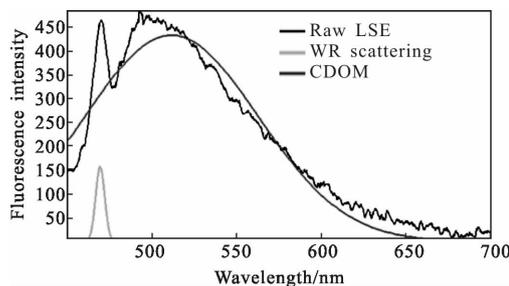
(a) Recognized two aquatic components
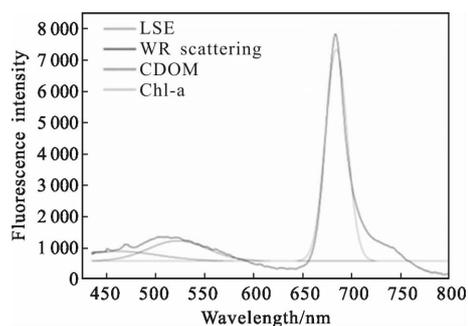
(b) Recognized three aquatic components

Fig.4 De-convolution of spectra with different numbers of aquatic spectral components

1.3 Calibration for fluorescence data

Fluorescence usually diminishes with increasing temperature. Recent studies revealed that temperature calibration is a necessary and important aspect of CDOM monitoring using in-situ fluorescence sensors, and a function （Eq. (2)） that can be used to standardize CDOM measurements to any reference temperature:

$$I(T) = I(T_0)[1 + \rho(T - T_0)] \tag{2}$$

where $I(T_0)$ is the reference temperature fluorescence intensity, ρ is the temperature coefficient, and $I(T_0) \times \rho$ is equal to the slope of fluorescence intensity versus temperature.

The temperature-corrected equation is derived when the raw data are adjusted to a reference temperature of T_0:

$$I(T_0) = I(T)/[1 + \rho(T - T_0)] \tag{3}$$

The influence of temperature change on determined concentration of CDOM in water was investigated in laboratory and the laser fluorometer instrument was used for the experiments. A beaker

with lake water was first cooled to ~20 ℃ in a dark refrigerator and then transferred to a dark incubator (HHS−1, Changfeng Tech), where they were gradually warmed to ~40 ℃ over a period of 1 to 2 h (with constant stirring). CDOM fluorescence and water temperature were simultaneously logged at 1 −min interval as the beaker was warmed.

Temperature effects on CDOM fluorescence normalized by WR scattering (Raman units, nm^{-1}) are presented in Fig.5. A linear fit of the normalized fluorescence intensity versus temperature yields a mean value of the slope of −0.001 1/℃ and the temperature coefficient, ρ, was estimated to be −0.027 6 at our chosen reference temperature of 20 ℃.
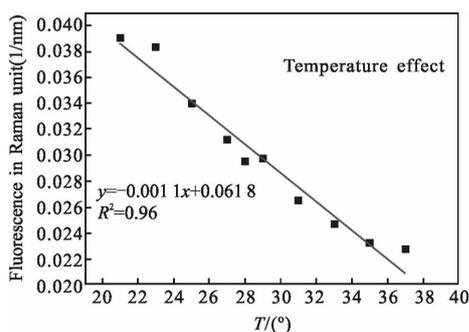

Fig.5 Temperature effect on CDOM fluorescence in Raman units

Figure 5 shows how the temperature effect is removed when the raw data are adjusted to a reference temperature of 20 ℃ using Eq.(2), where $\rho=$ −0.027 6. We can see that after using this value for ρ in Eq. (2), the effect of temperature could be removed from the raw lab data (Fig.6).
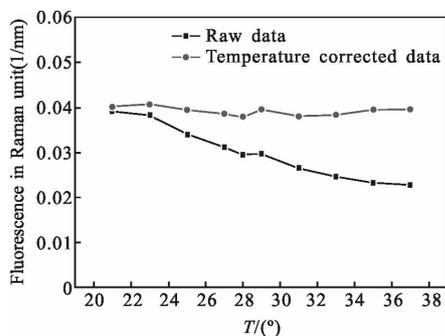

Fig.6 Temperature effect removed when the raw data are adjusted to a reference temperature of 20 ℃

2 Results and discussion

Laboratory and in-situ studies with the laser fluorometer were carried out in the estuarine zone and coastal zone of the East China sea (ECS) in April 2013. CDOM fluorescence, absorption, PH, temperature, turbidity, and salinity were measured simultaneously. Figure 7 shows the transect measurements stations in the estuarine and coastal region (distinguished by salinity in Fig.7). A total of 24 discrete samples were taken from the surface water. Temperature, turbidity, PH and salinity were obtained by a multi-parameter water quality monitor (Manta, Eureka) during the cruise. The absorptions of samples were analyzed in a spectrophotometer (PerkinElmer Lambada 35, Shimadzu) after the cruises, approximately three days after sampling.
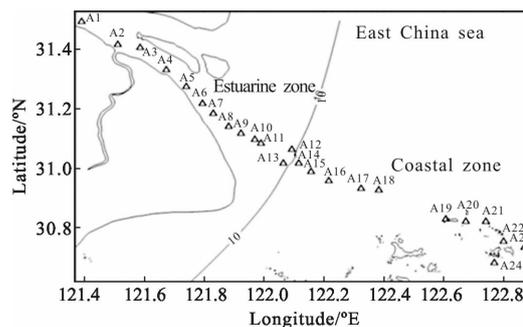

Fig.7 Distribution of transect measurement stations in the ECS in April 2013

To evaluate the laser fluorometer capacity for quantitative assessment of CDOM monitoring, the fluorescence spectra are compared with CDOM absorption analysis. The entire fluorescence dataset collected in the ECS is plotted against CDOM absorption dataset at each measurement station. The spectra of fluorescence and absorption measured can be seen in Fig.8(a) and Fig.8(b). Fig.8(a) shows the LSE spectral of field measurements. It reveals the LSE spectral variability in diverse water types. Absorption coefficient measurements in laboratory are presented in Fig.8 (b), showing the tendency of

gradually decreasing from estuarine to coastal zone of the ECS. Figure 8 shows typical LIF spectra of water recorded by the laser fluorometer at the excitation of 405 nm, illustrating some characteristic spectral features of LSE signatures. It illustrates that the peak at 470 nm corresponds to the water Raman scattering peak, the spectral peak nearby 500 nm corresponds to the CDOM fluorescence peak. In this paper, we mainly extracted the CDOM fluorescence spectra component and the water Raman scattering component was used to normalize the CDOM fluorescence.
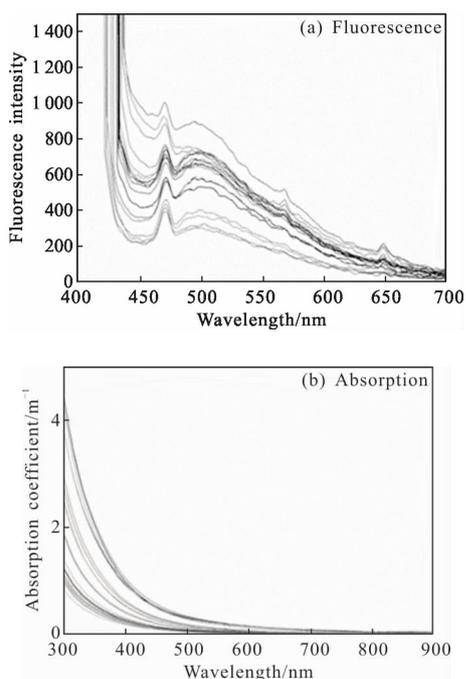

Fig.8 Spectrum of fluorescence and absorption (Stations 1 to 24)

Gaussian fitting was employed to de-convolute the fluorescence spectra, the de-convoluted CDOM component fluorescence spectra were presented in Fig.9(a). It show that the CDOM fluorescence spectra has a broad spectrum with no absolutely fixed fluorescence peak. In this experiment, the fluorescence peak was nearby 500 nm. A temperature calibration method by Patsayeve was used for correcting fluorescence data (Fig.9(b)) and 20 ℃ was chose as reference temperature (Eq. (3)). It demonstrated that fluorescence intensity overall decreased from field measured temperature (17.8 ℃) to reference temperature
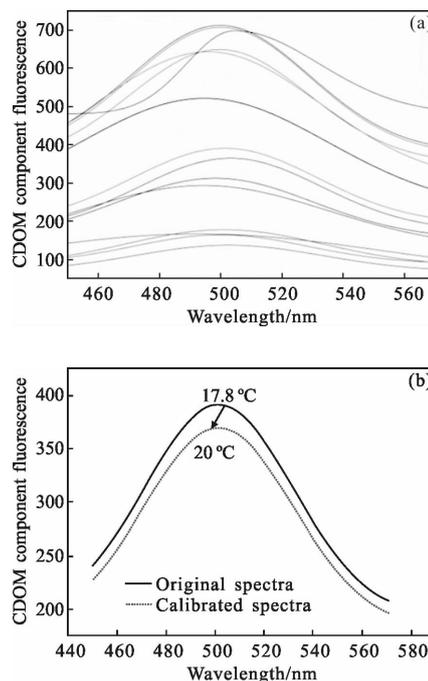
(20 ℃).

Fig.9 (a) De-convolution of the CDOM component spectra using SFS technique; (b) Calibration of CDOM fluorescence data at station A10 by Patsayeve approach

Correlation analyses between the CDOM fluorescence and a_{440} (absorption coefficient at 440 nm, stations 1 to 24) before and after using temperature calibration approach were present in Fig.10 (a) and Fig.10 (b). CDOM fluorescence intensity shows significant positive correlation with the UV – spectrophotometer assessment of CDOM absorption in a range of water types surveyed during the laser fluorometer field deployments. For example, Fig.10(a) displays the linear correlation of $R^2 = 0.81$ between fluorescence and the spectrophotometer measurements of a_{440} at all stations in the ECS. Figure 10(b) displays
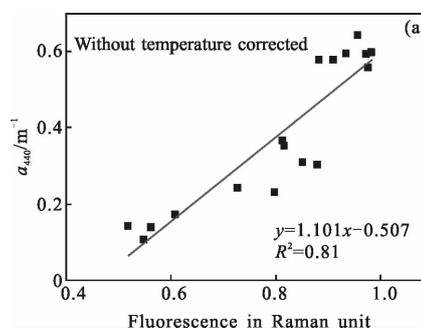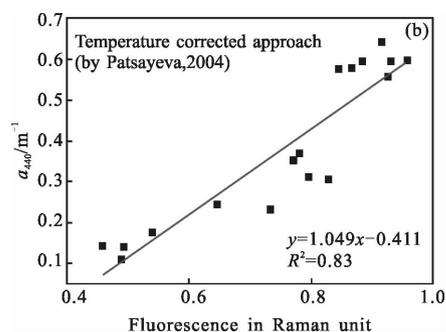
Fig.10 Correlation between the fluorescence and a_{440} (Stations 1 to 24) before and after using temperature calibration approach

the linear correlation of $R^2 = 0.83$ after using the temperature calibration algorithm by Patsayeva in 2004.

The result of improved linear correlation demonstrates that temperature calibration is effective for fluorescent sensor. The correlation between fluorescence and a_{440} demonstrates that the laser fluorometer provides effective and significant result for CDOM assessment with using the temperature calibration method. Additional consideration and work should be carried out when measuring the water with higher amounts of suspended solids.

Differences in values and correlations were found between sample sites for each of the two variables tested (absorption, fluorescence) in Fig.10. This was expected as these sites had different CDOM concentration. The concentrations of CDOM fluorescence (0.82−0.98; in April 2013), and a_{440} (0.35−0.64 m^{-1}; in April 2013) were found in the downstream section of the Yangtze River, relative to CDOM fluorescence (0.51−0.85; April 2013) and a_{440} (0.11−0.31 m^{-1}; April 2013) in the coastal region of the ECS. Distributions of CDOM fluorescence and a_{440} revealed similar gradual downward trends of magnitudes in the ECS, as water flowed down the Yangtze River and into the coastal zone of the ECS. A dilution process was detected as water flowed down the Yangtze River and into the ECS.

Fitting Gaussian of the least square method (de-convolution during SFS analysis) used in this study provides a satisfactory fit of the spectrum resulting from their summation to the LSE signal in the selected spectral range, and an overlap of aquatic spectral components has been well separated. However, problems may exist since the fitting method is unsuitable to the spectrum curve in high turbid water. So, diverse appropriate fitting methods should be designed for diverse curves of spectrum in different water types.

The laser fluorometer used a selective wavelength laser excitation (405 nm) and hyper-spectral CCD camera, integrated with SFS analysis to allow de-convolution of the overlapped emission bands of aquatic constituents, in addition with temperature calibration method to remove the effect on fluorescence measurements of multi-day trends in water temperature. Real-time information about intensity and spectral variability in CDOM fluorescence could be obtained from this instrument. However, it should be taken into consideration that there are limitations when using any fluorescence method as a water quality analysis tool. For example, not all portions of CDOM have fluorescence properties; therefore, the non-fluorescing portions are not included in the data analysis process, which can be problematic as those portions often contain revealing information about the sample. Also, in waters the amount of scattering is dependent on the water characteristics of the sample being studied; thus, the medium scatters most energy in the form of Mie scattering, and some energy in the form of Raman scattering; the rest of the energy is scattered according to the pigments in the water column. These factors give fluorescence a high unpredictability and make it difficult to compare different water bodies with different water quality characteristics. So, corresponding strategies should be developed to solve specific problems under specific environment and conditions, such as pre-filters arranged for extremely muddy water and additional measurements for

background signals to improve the SNR, etc.

3 Conclusion

The main goal of this study was to test applicability of the laser fluorometer in determining CDOM levels in estuarine and coastal areas of the ECS, and to verify and establish correlations between CDOM fluorescence and absorption laboratory analysis. We hypothesized that SFS fluorescence values would be significantly ($p < 0.05$), positively, linearly correlated to absorption measurements taken from water samples. During the laser fluorometer development, we first focused on designing a portable and flexible LIF fluorometer in a position to obtain broad high-resolution spectral fluorescence signal on the spot, and then acquired a set of field observations representing diverse water types; afterwards, we concentrated on thorough analysis of the laboratory and field measurements to develop new analytical algorithms, with effective SFS analysis and temperature calibration algorithm. There is still much work to do to make the instrument more reasonable. In particular, salinity and PH effects on SFS spectra need to be studied with more laboratory experiments, as additional parameters in the current temperature calibration method. Estuaries are unique in that they encompass areas influenced by both terrestrial and marine forces. Conditions are affected not only by seasonal changes and diurnal variability that influence all marine systems, but also by tides, multiple inputs of marine and terrestrial sources and fluctuating river flows. Lot of work still needs to be carried out to fully study the characteristics of CDOM in estuaries. Spectral correction results in significant change in the broadband spectral distribution of the LSE signal, spectral correction for the instrument will be further investigated. A linear tuning filter will be used to cut off the elastic scattering to remove the effect of elastic scattering on CDOM fluorescence soon. It has been shown that sometimes there are quantitative discrepancies between in-situ fluorescence data and laboratory analysis in some regions. Qualitatively, however, we have determined that the laser fluorometer is a useful and efficient tool for establishing relative CDOM levels in aquatic environment. The laboratory and filed result demonstrated the possibilities of CDOM monitoring in real time based upon the laser fluorometer.

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